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Preparation and electrical properties of $0.4Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.6Pb(Zr_{0.4}Ti_{0.6})O_3$ thin films by 2-step annealing method

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Abstract Films of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPb(Zr_{0.4}Ti_{0.6})O_3$ ($x = 0.6$, 40PZN-60PZT) were deposited on Pt/TiO_2/SiO_2/Si substrate through spin coating. Using a combination of homogeneous precursor solution preparation and two-step pyrolysis process, we were able to obtain the 40PZN-60PZT thin films of perovskite phase virtually without pyrochlore phase precipitation after annealing above 650°C. But since annealing done at the high temperatures for extended time can cause diffusion of Pt, TiO_2 and Si, and precipitation of nonstoichiometric PbO, we adopted 2-step annealing method to circumvent these problems. The 2-step annealed films show dense microstructure than the 1-step films annealed at higher temperature. Furthermore, the root-mean-square surface roughness of 220 nm thick films which are annealed at 720°C for 1 min and then annealed at 650°C for 5 min was found to be 3.9 nm by atomic force microscopy as compared to the 12 nm surface roughness of the film annealed only at 720°C for 5 min. The electrical properties of 2-step annealed films are virtually same and those of the 1-step annealed films annealed at high temperature. The film 2-step annealed at 720°C for brief 1 min and with subsequent annealing at 650°C for 5 min showed a saturated hysteresis loop at an applied voltage of 5 V with remanent polarization (P_r) and coercive voltage (V_c) of 25.3 μC/cm^2 and 0.66 V respectively. The leakage current density was lower than 10^{-5} A/cm^2 at an applied voltage of 5 V.

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1 Introduction

Relaxor ferroelectrics and their solid solutions have attracted much attention recently because of their excellent combined dielectric and electromechanical properties [1, 2]. $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and its solid solutions belong to this ferroelectric group [2–4]. But polycrystalline ceramic PZN, which has perovskite structure, without other phase precipitation is very difficult to prepare by conventional solid state reaction [5, 6] due to the unfavorable tolerance factor and the large difference of electronegativity [7]. So there has been many studies to stabilize PZN by partial substitution of A or B site cations such as $PbTiO_3$ and $BaTiO_3$ [8–10]. In this study, we chose a well-known ferroelectric material $Pb(Zr_{0.4}Ti_{0.6})O_3$ as solid solution stabilizer for PZN.

Relaxor ferroelectric thin films and its solid solutions need high annealing temperature to develop perovskite structure [5, 11]. But high temperature and long time annealing on Si substrate cause deterioration of electromechanical properties due to the Pt, TiO_2, Si inter-layer reaction or diffusion and nonstoichiometry problem by PbO evaporation. As previously reported, annealing temperature is more dominant factor than annealing time, and nucleation takes phase, within only a second at phase formation temperature [12]. Namely, the activation energy of nucleation is higher than the activation energy of growth. This means that grain growth is possible at lower temperature than at nucleation temperature. So we introduced a 2-step annealing method in which annealing is conducted high temperature for short time(1 min) for nucleation and for grain growth is conducted for extended time(5 min) at lower temperature. In this study, we compared the properties of 2-step annealed films with those of 1-step annealed films. Both types of films show single perovskite phase without any pyrochlore precipitation.

2 Experiment

40PZN-60PZT thin films were spin coated on $Pt/TiO_2/SiO_2/Si$ substrates by sol-gel method. Lead acetate trihydrate $[Pb(CH_3CO_2)_2 \cdot 3H_2O]$, zinc acetate dihydrate $[Zn(CH_3CO_2)_2 \cdot 2H_2O]$, niobium ethoxide $[Nb(C_2H_5O)_5]$, zirconium isopropoxide $[Zr(OCH(CH_3)_2)_4]$, titanium isopropoxide $[Ti(OCH(CH_3)_2)_4]$ were used as starting materials and 2-methoxyethanol was used as solvent. Lead acetate trihydrate and zinc acetate dihydrate were dissolved separately and dehydrated in acetic anhydride. To compensate for lead and zinc loss during the thermal annealing, excess 15 mol% lead and 5 mol% zinc were added to the precursor solution. Deposition of the ferroelectric films on $Pt/TiO_2/SiO_2/Si$ was carried out by spin-coating technique at 2500 rpm for 40 s. The resulting film was pyrolyzed on a hot-plate for 5 min at 250°C and then 5 min at 400°C, respectively. After the 2-step pyrolysis, rapid thermal annealing was carried out on the films in 1-step and 2-steps. X-ray diffraction (XRD) and scanning electronic microscopy (SEM) were conducted to analyze the phase and the microstructure. The surface topography of the films was characterized by atomic force microscopy (AFM) on a Seiko SPA 400. For electrical measurements, Pt top electrode ($0.0003\ cm^2$) was deposited by sputtering method and annealed 5 min at 600°C. The polarization-voltage (P-V) hysteresis loops and current density-voltage (I-V) curves were measured on a RT66 A ferroelectric test system and the capacitance-voltage (C-V) curves were measured on an HP4192 A at 100 kHz.

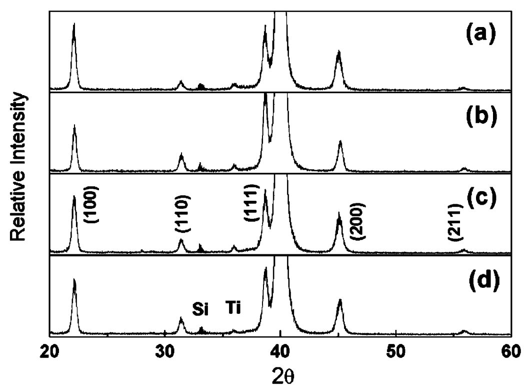


Fig. 1 X-ray diffraction patterns of 40PZN-60PZT films on $Pt/TiO_2/SiO_2/Si$ substrates annealed by RTA (a) at 650°C for 5 min, (b) at 720°C for 5 min, (c) initially at 700°C for 1 min and subsequently at 630°C for 5 min, (d) initially at 720°C for 1 min and subsequently at 650°C for 5 min

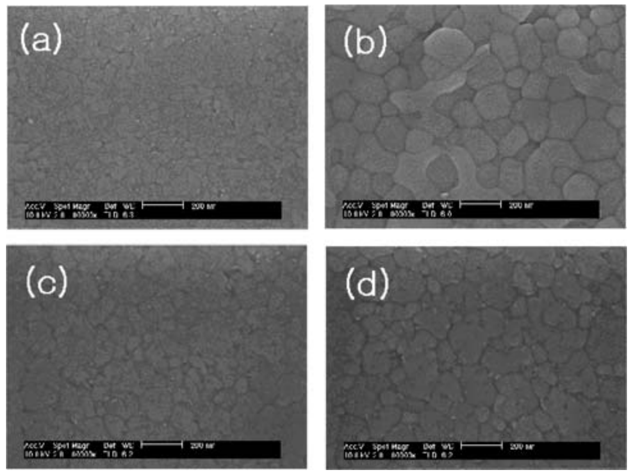


Fig. 2 In-plane view SEM micrographs of 40PZN-60PZT films annealed by RTA (a) at 650°C for 5 min, (b) at 720°C for 5 min, (c) at 700°C for 1 min and subsequently at 630°C for 5 min and (d) at 720°C for 1 min and subsequently at 650°C for 5 min

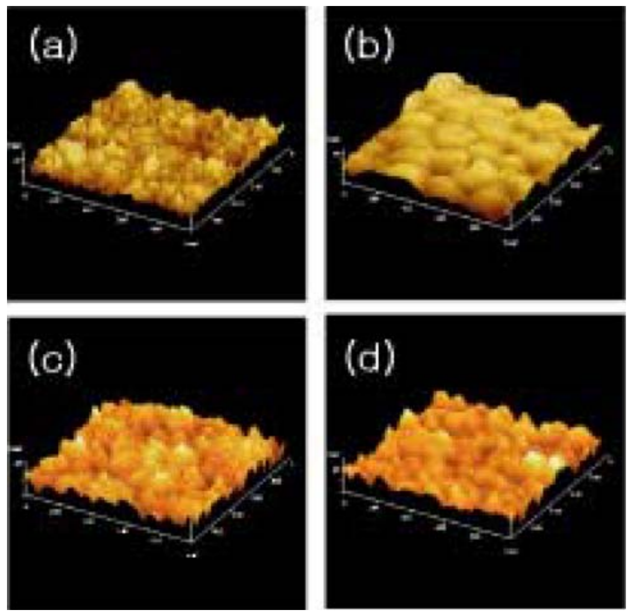


Fig. 3 The AFM picture of 40PZN-60PZT films annealed (a) at 650°C for 5 min, (b) at 720°C for 5 min, (c) at 700°C for 1 min and subsequently at 630°C for 5 min, (d) at 720°C for 1 min and subsequently at 650°C for 5 min by RTA

3 Results and discussion

Figure 1 shows a series of the XRD patterns of 220 nm thick 40PZN-60PZT films crystallized above 650°C on a $Pt(150\ nm)/TiO_2(30\ nm)SiO_2/Si$ substrate. The films annealed by rapid thermal annealing (RTA) in 1-step (a) at 650°C, (b) at 720°C for 5 min, and in 2-step (c) at 700°C for 1 min and then at 630°C for 5 min, and (d) at 720°C for 1 min and at 650°C for 5 min. All the 40PZN-60PZT films show pure perovskite phase without pyrochlore precipitation and have random orientation. Figure 1(c) also shows single

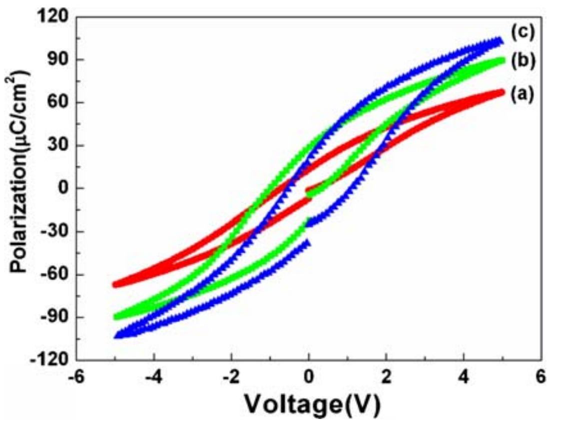


Fig. 4 Polarization-voltage (P-V) hysteresis curves of 40PZN-60PZT films 1-step and 2-step annealed (a) at 650°C for 5 min, (b) initially at 720°C for 1 min and subsequently at 650°C for 5 min and (c) at 720°C for 5 min

perovskite phase although it was annealed at a lower temperature. So we can reach a tentative conclusion that high annealing temperature for nucleation is quite important and low temperature annealing for growth can be implemented quite readily. Hence this 2-step annealing method is helpful for high temperature annealing. Both 1-step and 2-step films show random texture.

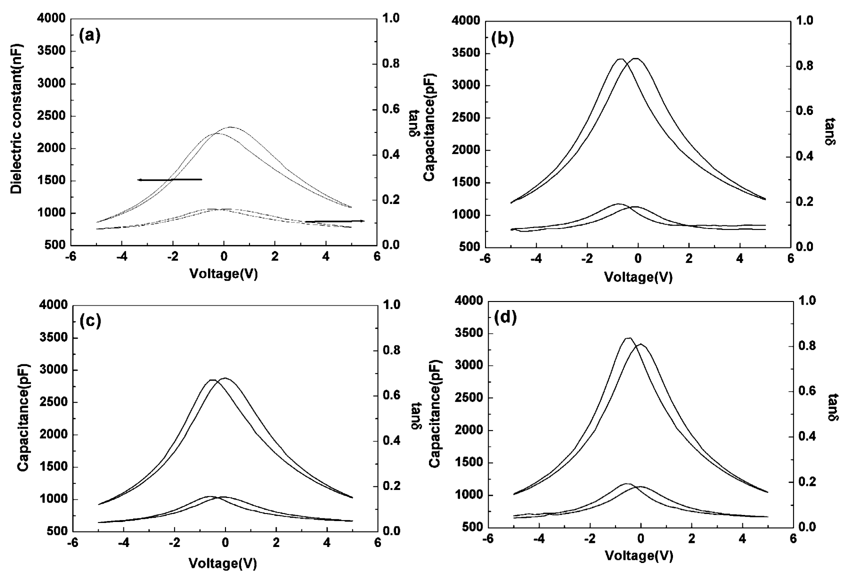
In-plane SEM micrographs of ferroelectric film layers are shown in Fig. 2. They all reveal no cracks. Their microstructure is strongly affected by annealing temperature. When the annealing temperature in 1-step process is increased from 650°C to 720°C, their grain size rapidly increases as well (compare Figs. 2(a) and (b)). Dense surface morphology is important because of the microstructure of films affect the electromechanical properties [13, 14]. The film 2-step annealed at 650°C for 5 min after initial 720°C 1 min annealing (Fig. 2(d)) has denser and smaller grains than the 1-step annealed film (Fig. 2(b)).

Three-dimensional AFM topography image of ferroelectric films (Fig. 3) also displays corresponding tendency. The root-mean square (rms) surface roughness of the 1 μm × 1 μm region is 12.3 nm with the maximum peak-to-valley (P-V) height of 91 nm for the specimen 1-step annealed at 720°C (Fig. 3(b)). However, the specimen 2-step annealed at the same temperature (Fig. 3(d)) has lower rms and P-V values: 3.9 nm and 28.7 nm respectively. Through comparison of the SEM and AFM results, the 2-step annealing is shown to be very useful to improve the morphology of film surface.

Polarization vs. electric field hysteresis curves of 220 nm thick PZN-PZT thin films annealed at various temperatures as a function of voltage are given in Fig. 4. The saturated polarization indicates that the films are ferroelectric. 2-step films annealed at 650°C for 5 min after initial 720°C 1 min annealing display the remanent polarization ($|P_r - P_r^*|/2$) and coercive voltage ($|V_c - V_c^*|/2$) values of 25.3 μC/cm^2 and 0.6 V respectively at an applied voltage of 5 V (Fig. 4(b)). These values are higher than those of the specimen 1-step annealed at 650°C for 5 min: 10.3 μC/cm^2 and 0.4 V. The former has the values similar to those of the 1-step specimen annealed at 720°C for 5 min: 29 μC/cm^2 and 0.8 V respectively.

The capacitance vs. voltage curve is shown in Fig. 5. This curve was measured at 100 kHz while dc bias voltage is applied from −5 V to 5 V back and forth by the rate of ±0.1 V. The 2-step annealed films at 650°C for 5 min after initial 720°C annealing for 1 min show its capacitance value about 3,390 pF. But the films annealed at 650°C for 5 min display show its value at much lower ∼2,230 pF and the films annealed at 720°C for 5 min in 1-step display somewhat higher value at ∼3,420 pF than that of the 2-step annealed specimen

Fig. 5 Capacitance-voltage (C-V) curves of 40PZN-60PZT films annealed (a) at 650°C for 5 min, (b) at 720°C for 5 min, (c) initially at 700°C for 1 min and subsequently at 630°C for 5 min, (d) at 720°C for 1 min and subsequently at 650°C for 5 min by RTA



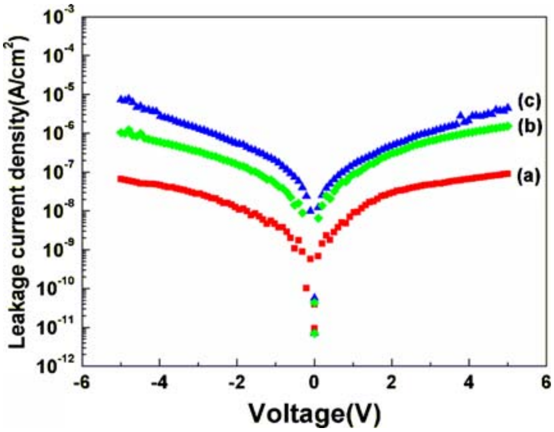


Fig. 6 Current density-voltage (J-V) curves of 40PZN-60PZT films 1-step and 2-step annealed (a) at 650°C for 5 min, (b) 2-step annealed initially at 720°C for 1 min and subsequently annealed at 650°C for 5 min and (c) 1-step annealed at 720°C for 5 min

of Fig. 5(d). The measured capacitance values of the specimen annealed at 650°C for 5 min after initial 720°C annealing for 1 min and those of the specimen annealed at 720°C for 5 min films show no significant difference. The obtained tanδ is below 0.2% for both types of the films.

Figure 6 is the leakage current density vs. voltage curves for the PZN-PZT thin films annealed at various temperatures. The leakage current density of the 2-step annealed film at 720°C for 1 min and subsequently at 650°C for 5 min is slightly better than the one 1-step annealed at 5 min 720°C. The specimen 1-step annealed at 650°C has the lowest leakage current density better by 0.5–1.0 order over the rest. The slight asymmetry of P-V, C-V and J-V curves may result from charge accumulation at the ferroelectric/electrode interface [15, 16].

4 Conclusion

Films of $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPb(Zr_{0.4}Ti_{0.6})O_3$ ($x = 0.6$, 40PZN-60PZT) were successfully deposited on $Pt/TiO_2/SiO_2/Si$ substrate above 650°C. But annealing done at high temperature for extended time can cause diffusion of Pt, TiO_2, Si and precipitation of nonstoichiometric PbO. To prevent the harmful reactions happening, we introduced a 2-step annealing method. The morphology of the specimen 2-step annealed at 720°C for 1 min and subsequently at 650°C for 5 min is better than that of the one 1-step annealed at 720°C for 5 min. The electrical properties of the 2-step processed specimen have slightly better overall properties. Dense microstructure and prevented harmful reaction which brought from 2-step annealing method improve electrical properties. So our 2-step annealing method is more efficient method to prepare the PZN-PZT capacitor. In this work, we have also shown that viable PZN-PZT solid solution thin film may be prepared.

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